

## DECARBOXYLATION AND COUPLING REACTIONS OF COAL STRUCTURES

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### ABSTRACT

Coupling reactions resulting from decarboxylation have long been associated with the retrograde reactions that hinder the pyrolysis and liquefaction of low-rank coals. The precise chemistry responsible for the coupling has not been proposed, beyond the suggestion that radical recombination or addition must be involved. We have performed a series of decarboxylation/coupling experiments in monomeric benzoic acid systems under liquefaction-relevant, but homogeneous, reaction conditions. The principal findings whose implications will be discussed are: (1) coupling as a result of decarboxylation tends to be very minor (generally < 10%); (2) under strongly oxidizing conditions, namely the absence of scavengers and the presence of one-electron oxidants (which may pertain to the interior of coal particles during the early part of liquefaction), coupling can be as much as 50% of the decarboxylations; (3) amine bases tend to promote decarboxylation but either inhibit or do not affect coupling; (4) H-donors inhibit coupling and, in some circumstances, decarboxylation induced by one-electron oxidants. The limited coupling associated with decarboxylation under most of these liquefaction-related conditions suggests that coupling associated with phenols may be more important.

### INTRODUCTION AND OBJECTIVES

It has become increasingly clear in recent years not only that retrograde reactions substantially hinder the liquefaction of low-rank coals, but also that oxygen functional groups in the coal structure are major actors in these retrograde reactions. Carboxyl functions have been implicated in the crosslinking of coals during heating at relatively low temperatures,<sup>1,2</sup> and Serio et al.<sup>3</sup> have been able to model the pyrolytic loss of solvent swelling by including one additional crosslink in the network for every CO<sub>2</sub> evolved. Moreover, pretreatments that have been found to be effective in promoting liquefaction have also shown a corresponding decrease in the early CO<sub>2</sub> evolution.<sup>4</sup> Thus, although crosslinking is correlated with the evolution of CO<sub>2</sub> and H<sub>2</sub>O and it therefore seems that carboxyl and/or phenolic groups are involved, we do not know exactly how or why. In order to best mitigate the retrograde reactions it is necessary to better understand their mechanisms—i.e., to know what factors promote and inhibit them.

A recent study by Siskin and coworkers<sup>5</sup> showed that decarboxylation of naphthoic acid under hydrothermal conditions was attended by formation of some binaphthyl, but the coupling aspect was not elaborated in that paper. As a prelude to studies with polymeric compounds, we have carried out and report here on a series of experiments with coal-related monomeric carboxylic acids. We have examined rates of decarboxylation and coupling to see if crosslinking results directly from decarboxylation, as well as how crosslinking is affected by ion exchange, the presence of a hydrothermal environment, and other conditions relevant to pretreatment.

### EXPERIMENTAL

**Procedures.** Experiments on decarboxylation and coupling of monomeric carboxylic acids were carried out in fused silica ampoules. Samples were degassed and sealed under vacuum, with each sample filling approximately one-half of the tube at room temperature. The sealed tube and an appropriate quantity of solvent for pressure equalization was placed in an outer jacket of stainless steel tubing capped with compression fittings. The reaction vessel was then immersed in a temperature-controlled molten-salt bath for the desired time, the tube removed and quenched in water. After cooling in liquid nitrogen to condense CO<sub>2</sub> and volatile organics, the ampoule was opened and the sample removed by pipet and repeated washing of the tube with solvent. An internal standard was

added and the sample analyzed by gas chromatographic analysis using a flame ionization or mass selective detector. Product quantitation was obtained using the FID analyses, with molar responses determined separately for those compounds for which we had authentic samples and estimated by comparison with similar species when no sample was available. Generally, at least three split injections of each sample were performed using an autoinjector. For most species the reproducibility was within  $\pm 2\%$  and we estimate the overall analytical accuracy to be within  $\pm 5\%$ . An exception pertains to the highly polar carboxylic acids, which exhibited excessive peak tailing in the gas chromatograms. These compounds showed much less reproducibility both from injection to injection and in the day-to-day variation in the molar response. For these species we estimate the overall analytical accuracy to be  $\pm 12\%$ .

**Chemicals.** Benzoic acid (99+% by GC analysis), o-Anisic acid (2-Methoxybenzoic acid, Aldrich, 99%), 3,4-Dimethoxybenzoic acid (Aldrich 99+%), 3-Methoxy-4-hydroxybenzoic acid (Aldrich 97%), m-Hydroxybenzoic acid (Aldrich 99%), Phenylacetic acid (99+% by GC analysis), Cupric acetate monohydrate  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}]$ , Fisher scientific] and  $\text{Fe}_3\text{O}_4$  powder (supplier unknown, particle size  $\sim 0.2 \mu\text{m}$ ) were used without further purification.

## RESULTS

**The Decarboxylation of Activated and Unactivated Benzoic Acids.** Table 1 shows the results obtained for a series of benzoic acids under typical "liquefaction" conditions, i.e.,  $400^\circ\text{C}$  in tetralin, sometimes with small amounts of other additives such as base.

Data in this table demonstrate that the decarboxylation of benzoic acid itself is slow at  $400^\circ\text{C}$  in tetralin (3-5% in 1 hr), unless a fairly strong base or other decarboxylation promoter is present. The substituted but unactivated substrate 3-hydroxybenzoic acid gives a similar degree of decarboxylation. Surprisingly, the decarboxylation of calcium benzoate in tetralin is no faster than that of the free acid. None of these compounds gave significant coupling, either with the starting acid, benzene, tetralin, or naphthalene. In cases where species with hydroxyl groups, e.g. naphthol, were present, there was a small amount (up to several percent) of esterification together with small amounts of the rearranged product of this ester. Since esters will not survive liquefaction conditions when water is present, as it typically is in coal liquefaction, we currently do not consider these "non-permanent" linkages to be of great importance with regard to retrograde reactions.

The near-absence of coupling, together with the slow decarboxylation of benzoic acid itself at  $400^\circ\text{C}$ , would make it appear that unactivated aromatic carboxylic acids do not represent the acid species that undergo facile decarboxylation between  $250^\circ$  and  $350^\circ\text{C}$  during the heating of low-rank coals. Therefore, we performed additional experiments to examine the behavior of benzoic acid derivatives known<sup>6,7</sup> to be activated toward decarboxylation via electrophilic attack. For all of these, except for meta hydroxy benzoic acid and veratric acid (3,4-dimethoxy benzoic acid, last row in Table 1), decarboxylation in tetralin was almost complete in one hour at  $400^\circ\text{C}$ . Again however, there was no substantial level of coupling products. (In some cases there were small chromatographic peaks, as yet unidentified, at higher retention times. We cannot rule out the possibility that these result from some type of coupling associated with decarboxylation, but in any case they amount to less than 5% at most of the decarboxylated acid.)

Perhaps the most interesting result with the activated acids is that obtained with veratric acid. This acid did *not* undergo complete decarboxylation, but was recovered in ca. 25% yield after 1 hour in tetralin at  $400^\circ\text{C}$ , in contrast to the analog containing a free -OH in the para position, which underwent complete decarboxylation. Because p-OMe is generally just as activating toward electrophilic attack as p-OH, the above difference indicates that the rate-determining step cannot simply involve attack on the starting material itself. That is, this result suggests that the principal mode of decarboxylation by electrophilic attack either involves reaction of the phenoxy anion or the keto form of the phenolic acid, which is accessible only through the free phenol. One possibility is that the keto form of the acid simply undergoes thermal unimolecular bond cleavage (homolysis) to yield a stabilized radical (phenoxy) and the radical  $\cdot\text{CO}_2\text{H}$ , in exact analogy to the thermal cleavage of benzyl and phenoxy

phenols that has been previously elucidated.<sup>8</sup> This possibility, however, is ruled out by the estimated enthalpy requirement for the reaction, which dictates that the decarboxylation would have a half-life of no less than 1000 hours at 400°C.

**The Effect of Electron-Transfer Agents and the Acceptor/Scavenger Ratio.** Having seen very little coupling resulting from decarboxylation of any of the acids tested thus far, we have broadened the range of reaction conditions under which these acids are being heated, in an attempt to bring about more coupling and perhaps approximate more closely conditions encountered in the thermal processing of low rank coals. Essentially this means reaction in more oxidizing systems, i.e. systems with potential oxidants for carboxylate ions, and with little or no hydro- or alkyl-aromatic. During the early stages of coal liquefaction, such relatively oxidizing conditions might be expected to arise in the interior portions of the coal which are not directly surrounded by the liquefaction solvent. Furthermore, under these conditions, literature data for the reactions of phenyl- and other aryl radicals<sup>11-13</sup> lead us to expect that any phenyl radicals formed will add very readily to essentially any aromatic system, displacing hydrogen to form biaryl linkages. For these experiments we used mixtures of benzoic acid and naphthalene as the basic system and then added various combinations of the reagents that were found from our previous studies to affect decarboxylation, particularly base (pyridine) and the electron transfer agents  $\text{Fe}_3\text{O}_4$  and  $\text{Cu}(\text{OAc})_2$ .

Table 2 shows the effects of the 1-electron oxidants  $\text{Fe}_3\text{O}_4$  and  $\text{Cu}(\text{OAc})_2$  and the solvent H-donating ability on the decarboxylation of benzoic acid. Both electron transfer agents markedly increase decarboxylation (from 3-5% as shown in Table 1 to at least ~50% as seen in Table 2). This increase is qualitatively in accord with the literature data on copper/amine-promoted decarboxylation.<sup>6,7</sup> Decarboxylation is at least ten times faster with  $\text{Cu}(\text{OAc})_2$  than with  $\text{Fe}_3\text{O}_4$ , but the generation of coupling products is about ten times faster in the presence of  $\text{Fe}_3\text{O}_4$ . In contrast to the experiments reported in Table 1, three main coupling products, phenylnaphthalenes, pyridinylnaphthalenes, and binaphthyls are now observed when either of the electron-transfer agents are present. The similarity of the products suggests that qualitatively similar chemistry is contributing in both systems. However, we still see only relatively low levels of coupling products, particularly in the  $\text{Cu}(\text{OAc})_2$  system.

The effect of the hydrogen donors on coupling and decarboxylation of benzoic acid can be seen by comparing the latter two experiments in Table 2. In these experiments with cupric acetate, the amount of coupling is decreased by 70% when naphthalene is replaced by a tetralin/1-methylnaphthalene/naphthol mixture. Both the decarboxylation rate and the ratio of coupling to decarboxylation decrease significantly. This result is suggestive that the primary mode of coupling involves aryl radicals, which are readily scavenged by any of the three new components. The most likely mode of aryl radical production is from  $\text{C}_6\text{H}_5\text{CO}_2^\bullet$ , which should rapidly decompose to  $\text{C}_6\text{H}_5^\bullet$  and  $\text{CO}_2$ . Interestingly, decarboxylation itself is also markedly slowed when an H-donor solvent is used, decreasing from  $\geq 83\%$  to about 47%. The reason for this is uncertain. Presuming decarboxylation involves  $\text{C}_6\text{H}_5\text{CO}_2^\bullet$ , thermochemical kinetic analysis indicates that the  $\text{C}_6\text{H}_5\text{CO}_2^\bullet$  radical should decarboxylate much more rapidly than it could abstract hydrogen from e.g. tetralin. It appears, therefore, that the H-donor must be interfering in some other manner with the activity of the electron transfer agent. (For example, a redox reaction within a cupric acetate molecule to produce cuprous acetate and  $\text{C}_6\text{H}_5\text{CO}_2^\bullet$  might possibly be interfered with by tetralin, which, as an added reducing agent might compete with the internal reducing agent, carboxylate anion.)

**Coupling Product Distribution.** A more detailed breakdown of products from benzoic acid under various conditions is provided in Table 3. The nature and distribution of the coupling products themselves may provide an indication of the factors limiting coupling under the above reaction conditions. GC/MS analysis has allowed us to identify the coupling products 1- and 2-phenylnaphthalene, two isomers of pyridinylnaphthalene, and the 1,1', 1,2', and 2,2'-binaphthyls, as listed in Table 3.

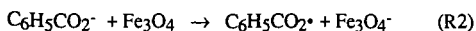
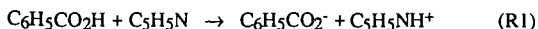
Typically the 1-phenylnaphthalene is two to three times more abundant than the 2-phenylnaphthalene, consistent with a radical mechanism and the relative rates of radical addition and H-transfer to naphthalene that have been reported in the literature.<sup>14,15</sup> In the case of the binaphthyls, the ratio of

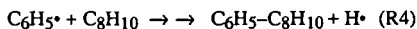
1,2'-, 1,1'-, and 2,2'-binaphthyl is typically 3:2:1. This product distribution is consistent with a statistical preference for the 1,2' isomer, a rather small (1-2 kcal/mol) preference for abstraction of the naphthalene 1-hydrogens,<sup>16</sup> and very little kinetic preference for the highly exothermic addition of an aryl radical to the favored<sup>14,15</sup> 1-position of another naphthalene. The least abundant isomer (2,2'-) represents addition of the least favored aryl radical to the least favored position for addition. The isomer distribution reported by Stein,<sup>16</sup> who studied binaphthyl formation starting from the pure hydrocarbons, differs slightly from our product distribution; he reported the 2,2' isomer to be slightly more favored than the 1,1' binaphthyl.

In the case of the pyridinylnaphthalenes, the point of connection of the pyridine to the naphthalene ring is inferred from the phenylnaphthalenes, but the connections to the pyridine ring are unknown. The pyridinyl- and naphthyl-naphthalene isomer distributions are generally consistent with those expected from H-abstraction from either pyridine or naphthalene by the initially produced phenyl radical, followed by addition of the new aryl radical to naphthalene. However, the formation of similar amounts of pyridinylnaphthalenes and naphthyl-naphthalenes (binaphthyls) is surprising in view of the fact that the reaction mixture contains seven times as much naphthalene as pyridine. In order to check our inference that these products result directly or indirectly from decarboxylation, we performed control experiments with mixtures of benzene, pyridine, and naphthalene in the presence of Fe<sub>3</sub>O<sub>4</sub>. Although no significant quantity of phenylnaphthalenes were formed, we surprisingly did find pyridinylnaphthalenes and binaphthyls. Their amounts indicate that perhaps 30-40% of the *secondary* coupling products could arise from mechanisms not involving decarboxylation as the original radical source. However, the *primary* coupling products (i.e., those between phenyl and naphthalene) are almost entirely due to decarboxylation.

**Rates of Decarboxylation and Coupling.** As would be anticipated from the data of Tables 1 and 2, the addition of 10 m% of pyridine to the naphthalene/benzoic acid mixture (Condition 1 to Condition 2) should increase decarboxylation, and it does increase it about a factor of four (to 19%). It does not, however, substantially affect the coupling to decarboxylation ratio, which drops slightly from 0.027 to 0.023. However, if 10 m% of Fe<sub>3</sub>O<sub>4</sub> is added instead of pyridine (Condition 1 to Condition 3), decarboxylation is increased by a factor of only two, while the coupling to decarboxylation ratio rises dramatically to 0.49. Apparently, the absence of a reducing agent such as tetralin and the presence of a 1-electron oxidant is necessary before coupling reactions become substantial. Finally, if pyridine is added along with the Fe<sub>3</sub>O<sub>4</sub>, decarboxylation is increased to ≥ 58%, but the ratio of coupling/decarboxylation ratio is reduced by two-thirds when compared to the Fe<sub>3</sub>O<sub>4</sub>-only case. Thus, although pyridine/Fe<sub>3</sub>O<sub>4</sub> synergistically promote decarboxylation, the base leads to an interruption or circumvention of the pathway responsible for coupling.

**Mechanistic implications.** Although there seem to be relatively few definitive mechanistic investigations of the decarboxylation unactivated acids, decarboxylations have been major synthetic reactions for many years, and the phenomenology is extremely varied, including what appear to be anionic, free radical, and molecular routes.<sup>5-7,9,10</sup> The decarboxylation products we have observed at high temperatures (>300°C) in more oxidizing systems (no donor solvent present, and with an added electron-transfer agent) tend to support one of the traditionally anticipated routes, outlined below, whereby the benzoic acid is converted to benzoate by the base (R1) and the benzoate anion to the radical by the electron transfer agent (R2). The carboxyl radical then decomposes to CO<sub>2</sub> and phenyl radical (R3). Phenylnaphthalenes result from net displacement of a naphthyl hydrogen by phenyl radical (R4). Alternatively, the phenyl radical can abstract hydrogen from pyridine or naphthalene prior to successful addition, resulting in pyridinyl and naphthyl radicals. Attack of these secondary radicals on naphthalene can then explain the formation of pyridinylnaphthalenes and binaphthalenes, as briefly indicated above. The important conclusion is that appearance of these secondary coupling products and the impact of tetralin described above suggest that any radical scavenger should be able to substantially prevent this mode of coupling.





It is interesting that a mechanism for the widely used copper/quinoline-promoted decarboxylation of aromatic acids was not published until 1970,<sup>7a</sup> and is still not entirely clear. It is thought to involve the formation of cuprous benzoate as a key intermediate, which then decomposes *without* the formation of a free aryl radical. Since reduction of cupric benzoate to cuprous benzoate can be accomplished by electron transfer from one of the benzoate moieties to the cupric ion, potentially releasing CO<sub>2</sub> and a phenyl radical, both radical and non-radical pathways may be accessible to different degrees and/or under different conditions (copper-quinoline promoted decarboxylations are usually carried out well below 300°C). Thus the scheme in Reactions 1 through 5 is almost certainly simplified and there is very likely more than one mechanism for transition-metal catalyzed decarboxylations operative for different substrates under different conditions.<sup>7,10</sup> In current experiments we are examining the behavior of some activated benzoic acids in the presence of iron oxide, as well as that for a prototypical aliphatic acid.

## SUMMARY

The rates of decarboxylation of benzoic acids range from a few percent in 1 hour at 400 °C for unactivated acids to > 98% for species activated in the ortho, para positions. Rates of decarboxylation can be increased by the addition of amine base and/or 1-electron oxidants, but our experiments demonstrate that coupling reactions of activated and unactivated monomeric carboxylic acids are generally *not* important under coal liquefaction conditions in the absence of electron transfer agents. The decarboxylation of the calcium salt of benzoic acid is not significantly faster than that of benzoic acid itself. This is in apparent contrast to the fact the calcium or magnesium forms of low-rank coals produce more CO<sub>2</sub> and show more evidence of crosslinking on heating.<sup>3,17,18</sup> Decarboxylation and coupling reactions of benzoic acid are induced by the electron transfer agents Cu(OAc)<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>, and under some highly oxidative conditions one coupling reaction can occur for every two decarboxylations. The rate of coupling in the presence of electron oxidants is greatly reduced by both base and H-donors such as tetralin. The overall conclusion is that, to the extent that monomeric species are representative of coal structures, rather selective conditions are necessary for decarboxylation to result in coupling during coal liquefaction. This suggests either that other mechanisms may be substantially responsible for the retrograde reactions associated with CO<sub>2</sub> evolution, or, if decarboxylation is involved, that it ought to be possible to interrupt these reactions by appropriate control of the conditions.

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Table 1. Decarboxylation of activated and unactivated benzoic acids.

Acid Structure	Solvent System <sup>d</sup>	Concentration m%	Reaction Time Hrs	% Decarbox- ylation	% Coupling <sup>a</sup>
PhCO <sub>2</sub> H <sup>b,c</sup>	Tet/THQ 75/20	5	1	4	<20
	Tet/THQ/H <sub>2</sub> O 55/20/20	5	1	5	<20
	Tet/PipPy 75/20	5	0.5	77	<3
	Tet/THQ/Zn(OAc) <sub>2</sub> 75/20	5	1	75	<5
	Tet/1-Naphthol 80/10	10	1	3	<2 <sup>e</sup>
	Ca(PhCO <sub>2</sub> ) <sub>2</sub> Tet/1-Naphthol 80/10	10	1	3	<2
4-OH-PhCO <sub>2</sub> H	Tet	20	1	>98	<3
3-OH-PhCO <sub>2</sub> H	Tet	10	1	2	-
2-OMe-PhCO <sub>2</sub> H	Tet	10	1	>98	<3
	Tet	20	1	>99	<3
	Tet/Pyrene	10	1	>99	<3
3-OMe-4-OH- PhCO <sub>2</sub> H	Tet	10	1	>99	<2
3-OMe-4-OMe- PhCO <sub>2</sub> H	Tet	10	1	~75	<3

- a. This figure should be considered an upper limit; it represents the sum of small unidentified high retention time peaks that are potential coupling products, given as a percent of decarboxylation. Thus larger values listed for cases where there is limited decarboxylation do not generally reflect larger absolute amounts of possible coupling products.
- b. The first four sets of data for benzoic acid itself are taken from previous work.
- c. For economy of space, the symbol "Ph" is used here to represent a single phenyl ring, regardless of whether there are 3, 4 or 5 unsubstituted positions on the ring.
- d. "THQ" represents 1,2,3,4-tetrahydroquinoline, "Tet" is tetralin, and "PipPy" is the strong organic base/nucleophile 4-piperidinopyridine.
- e. Does not include formation of naphthylbenzoate ester or rearranged product of this ester.

Table 2. Effects of different 1-electron oxidants and solvent H-donating ability on coupling and decarboxylation of benzoic acid<sup>a</sup>

BA (m%) <sup>b</sup>	Solvent System (m%) <sup>b</sup>	Results			
		%Rec. Acid	% Coupling <sup>c</sup>	% Decarbox. <sup>d</sup>	%(Coupl/Decarb)
11.3	Naph/Pyridine/Fe <sub>3</sub> O <sub>4</sub> 68.8/9.8/10.1	19.5	9.34	57.6	16.2
10.4	Naph/Pyridine/Cu Acetate 70.4/8.9/10.3	<0.1	2.96	83.4	3.5
9.8	Tet/MN/Naphthol/Cu Acetate 29.9/29.9/12.2/9.6/9.7	45.9	0.51 <sup>e</sup>	46.5	1.1

a. After reaction at 400°C for 1 hr.

b. BA = benzoic acid; Naph. = naphthalene; Tet = tetralin; MN = 1-methylnaphthalene; Naphthol = 1-naphthol; Cu Acet. = cupric acetate monohydrate [Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O].

c. As mol% of benzoic acid; refers to all peaks in the "coupling" region of the chromatogram.

d. Based on identified decarboxylation products including benzene and phenyl-containing coupling products.

e. This figure does not include 1% formation of naphthyl benzoate from benzoic acid and naphthol.

Table 3. Effect of Fe<sub>3</sub>O<sub>4</sub> and pyridine on decarboxylation and coupling of Benzoic acid during reaction in naphthalene at 400°C for 1 hour

Reactants	Condition 1 mol%	Condition 2 mol%	Condition 3 mol%	Condition 4 mol%
Benzoic Acid	9.57	10.00	10.13	11.26
Naphthalene	90.43	80.23	79.49	68.80
Pyridine	—	9.77	—	9.82
Fe <sub>3</sub> O <sub>4</sub>	—	—	10.38	10.11
<b>Products</b>				
Benzoic Acid	102.19	92.58	99.74	19.48
Naphthalene	99.80	99.89	98.38	96.08
Pyridine	—	78.88	—	87.54
Benzene	4.26	18.07	6.47	54.11
Naphthalene Impurities	0.77	0.76	0.75	0.76
Biphenyl <sup>a</sup>	< 0.004	< 0.004	< 0.004	0.14
1-Phenylnaphthalene <sup>a</sup>	0.058	0.23	2.36	2.20
2-Phenylnaphthalene <sup>a</sup>	0.055	0.20	1.02	0.99
1-Pyridinylnaphthalene <sup>a</sup>	—	< 0.004	—	2.45
2-Pyridinylnaphthalene <sup>a</sup>	—	< 0.004	—	0.90
1,1'-Binaphthalene <sup>a</sup>	< 0.004	< 0.004	0.91	0.79
1,2'-Binaphthalene <sup>a</sup>	< 0.004	< 0.004	1.44	1.44
2,2'-Binaphthalene <sup>a</sup>	< 0.004	< 0.004	0.44	0.43
% Decarboxylation <sup>b</sup>	4.4	18.5	9.9	57.6
%(Coupling/Decarbox.) <sup>b,c</sup>	2.7	2.3	48.5	16.2

a. Mol percentages are based on the benzoic acid reactant.

b. Based on identified products.

c. For the purposes of this table it is assumed that pyridinylnaphthalenes and binaphthyls are coupling products that stem from decarboxylation after a shift of the radical center from the initial phenyl radical to either pyridine or naphthalene (see text).